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TECHNICAL FIELD

[Field of the Invention] this invention relates to a multilayer-extrusion blow-molding method, the multilayer co-extruding method, a multilayer extension blow-molding method, the laminating method, and the dampproof multilayer-extrusion structure that it is further fabricated by the vacuum or the compressed-air method from a multilayer sheet, and can be used for a container, a bag, etc. still in detail about the dampproof multilayer-extrusion structure the steam barrier excelled [structure] in the fitness and shock resistance, and the dampproof hyperoxia barrier multilayer-extrusion structure.

PRIOR ART

[Prior art] Conventionally, as quality of the material for water vaporproofing packagings, the resin of polyolefine systems, such as polypropylene, is good in points, such as price, physical properties, and a moldability, and are used. [many] However, in the case of polypropylene, steam barrier nature is moisture permeation coefficient 0.3g and mm/m2 and 24hr (ASTMF1249), and is carrying out using together an inner bag or a drying agent (water-vapor-absorption agent) other than the packing fabricated with polypropylene etc. in the contents as which the steam barrier nature beyond the above is required, for example. In this gestalt, there were problems, such as confusion (for example, grade which mistakes for a tablet and is drunk by mistake) with the contents by being packaged excessively, and there being problems, like the eccrisis with the scarce simple nature at the time of use comes out mostly, or using a drying agent, and a life of a drying agent, by using an inner bag.

[0003] Moreover, there is a polyolefine which made 5-60 mols % of annular olefin components contain as a resin which excelled polypropylene in steam barrier nature so that degree of crystallinity may be 20% or less. However, in the aforementioned polyolefine independent, the moldability was bad and became only that to which shock resistance does not bear use deficiently further.

CLAIMS

[Claim]

[Claim 1] The dampproof multilayer-extrusion structure excellent in the shock resistance which consists of a resin configuration of at least three layers characterized by making the polyolefin resin layer which has 5-60 mols % of annular olefin components intervene between polyolefine system resin layers.

[Claim 2] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 1 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion

structure between the aforementioned polyolefine system resin layers.

[Claim 3] The dampproof multilayer-extrusion structure excellent in the shock resistance characterized by having at least one layer of adhesive resin layers between polyolefine system resin layers in the resin configuration of claim 1 publication.

[Claim 4] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 3 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the aforementioned polyolefine system resin layers.

[Claim 5] The dampproof multilayer-extrusion structure excellent in the shock resistance characterized by having at least one layer of gas barrier nature resin layers in the resin configuration of claim 1 publication.

[Claim 6] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 5 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the aforementioned polyolefine system resin layers.

[Claim 7] The dampproof multilayer-extrusion structure excellent in the shock resistance characterized by having at least one layer of adhesive resin layers between the resin layers which turn into the resin layer used as the outermost layer, and an innermost layer in the resin configuration of claim 5 publication.

[Claim 8] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 7 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the aforementioned polyolefine system resin layers.

[Claim 9] The dampproof multilayer-extrusion structure excellent in the shock resistance which consists of a resin configuration of at least four layers characterized by having a resin layer with a heat deflection temperature higher than the polyolefine system resin layer which is an innermost layer resin layer in a sealant lamination as a base-material layer which is the lamination and outer layer which consist of the dampproof multilayer-extrusion structure excellent in the shock resistance of claim 1 publication as a sealant layer.

[Claim 10] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 9 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the polyolefine system resin layers in the aforementioned sealant lamination.

[Claim 11] The dampproof multilayer-extrusion structure excellent in the shock resistance characterized by having at least one layer of adhesive resin layers between each resin layer in the resin configuration of claim 9 publication.

[Claim 12] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 11 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the polyolefine system resin layers in the aforementioned sealant lamination.

[Claim 13] The dampproof multilayer-extrusion structure excellent in the shock resistance characterized by having at least one layer of gas barrier nature resin layers between the polyolefine system resin layers in a sealant lamination in the resin

configuration of claim 9 publication.
[Claim 14] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 13 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the polyolefine system resin layers in the aforementioned sealant lamination.
[Claim 15] The dampproof multilayer-extrusion structure excellent in the shock resistance characterized by having at least one layer of adhesive resin layers between each resin layer in the resin configuration of claim 13 publication.
[Claim 16] The dampproof multilayer-extrusion structure excellent in the shock resistance of the claim 15 publication characterized by having at least one layer of the layers which contain the recycling material of the aforementioned dampproof multilayer-extrusion structure between the polyolefine system resin layers in the aforementioned sealant lamination.
[Claim 17] The dampproof multilayer-extrusion structure excellent in shock resistance characterized by being multilayer sheet mold goods in the dampproof multilayer-extrusion structure given in the claim 1 or the claim 16.
[Claim 18] The dampproof multilayer container excellent in shock resistance which is the dampproof multilayer-extrusion structure given in the claim 1 or the claim 8, and is characterized by being fabricated using the vacuum forming of a multilayer sheet, a pressure forming, or the vaccum pressure sky molding technique.
[Claim 19] The dampproof multilayer container excellent in shock resistance which is the dampproof multilayer-extrusion structure given in the claim 1 or the claim 8, and is characterized by fabricating this dampproof multilayer-extrusion structure using the multilayer blow-molding technique.
[Claim 20] The dampproof multilayer container excellent in shock resistance which is the dampproof multilayer-extrusion structure given in the claim 1 or the claim 8, and is characterized by fabricating this dampproof multilayer-extrusion structure using the multilayer extension blow-molding technique.

DETAILED DESCRIPTION

[Detailed description]
[0001]
[Field of the Invention] this invention relates to a multilayer-extrusion blow-molding method, the multilayer co-extruding method, a multilayer extension blow-molding method, the laminating method, and the dampproof multilayer-extrusion structure that it is further fabricated by the vacuum or the compressed-air method from a multilayer sheet, and can be used for a container, a bag, etc. still in detail about the dampproof multilayer-extrusion structure the steam barrier excelled [structure] in the fitness and shock resistance, and the dampproof hyperoxia barrier multilayer-extrusion structure.
[0002]
[Prior art] Conventionally, as quality of the material for water vaporproofing packagings, the resin of polyolefine systems, such as polypropylene, is good in points, such as price, physical properties, and a moldability, and are used. [many] However, in the case of polypropylene, steam barrier nature is moisture permeation coefficient 0.3g and mm/m2

and 24hr (ASTMF1249), and is carrying out using together an inner bag or a drying agent (water-vapor-absorption agent) other than the packing fabricated with polypropylene etc. in the contents as which the steam barrier nature beyond the above is required, for example. In this gestalt, there were problems, such as confusion (for example, grade which mistakes for a tablet and is drunk by mistake) with the contents by being packaged excessively, and there being problems, like the eccrisis with the scarce simple nature at the time of use comes out mostly, or using a drying agent, and a life of a drying agent, by using an inner bag.

[0003] Moreover, there is a polyolefine which made 5-60 mols % of annular olefin components contain as a resin which excelled polypropylene in steam barrier nature so that degree of crystallinity may be 20% or less. However, in the aforementioned polyolefine independent, the moldability was bad and became only that to which shock resistance does not bear use deficiently further.

[0004]

[Object of the Invention] this invention is made in order to solve the trouble of the above, conventional techniques, and in the structure for water vaporproofing packagings, it excels in shock resistance, and the multilayer-extrusion structure which excelled the structure which consists of a resin of polyolefine systems, such as further conventional polypropylene, in dampproofing and a multilayer container or the multilayer-extrusion structure excellent in moisture-proof hyperoxia barrier nature, and a multilayer container are offered.

[0005]

[The means for solving a technical problem] this invention is the dampproof multilayer container fabricated using the dampproof multilayer-extrusion structure and it excellent in the shock resistance which considers the resin configuration of at least three layers as a basic configuration which made the polyolefin resin layer which has 5-60 mols % of annular olefin components intervene between polyolefine system resin layers.

[0006] Hereafter, it explains still in detail. The important characteristic feature in the dampproof multilayer-extrusion structure excellent in the shock resistance by this invention is that it uses the polyolefine which has 5-60 mols % of annular olefin components as an interlayer. the polyolefine which has this annular olefin ****** -- hydrogen and carbon **** -- **** -- the becoming resin of a polyolefine system -- it is -- in addition -- and the cyclic structure which checks the crystal structure to the principal chain skeleton or a side chain and an umbrella -- although factors, such as high structure, should just exist, the resin "an annular polyolefine copolymer" of the polyolefine system which has an annular polyolefine component is preferably used for the chief examiner skeleton

[0007] As an annular olefin component, for example Bicyclo (2.2.1) hept-2-**** or its derivative, Tetracyclo (4. 4.0. 12 and 5 . 17, 10)-3-dodecen or its derivative, Hexa cyclo (6. 6.1.13, 6.110, 13.02, 7. 09, 14)-4-heptadecene or its derivative, Octacyclo (8. 8.0. 12 and 9 . 14 and 7 . 111 and 10 . 113 and 16 . 03 and 8 . 012 and 17)-5-******** or its derivative, ****** cyclo (6. 6.1. 13 and 6 . 02 and 7 . 09, 14)-4-hexa decene or its derivative, ****** cyclo (6. 5.1. 13 and 6 . 02 and 7 . 09, 13)-4-pentadecene or its derivative, Heptacyclo (8. 7.0. 12 and 9 . 14 and 7 . 111 and 16 . 03 and 8 . 012 and 16)-5-********** or its derivative, Tricyclo (4. 4.0. 12 and 5)-3-undecene or its derivative, Tricyclo (4. 3.0. 12 and 5)-3-decene or its derivative, Cyclo [****** / -4] (6.

5.1.13, 6. 02 and 7 . 09, 13), 10-****** deca diene, or its derivative, ****** cyclo (4. 7.0.12, 5.08, 13. 19, 12)-3-pentadecene or its derivative, Heptacyclo (7. 8.0. 13 and 6 . 02 and 7 . 110 and 17 . 011 and 16 . 112 and 15)-4-ray ****** or its derivative, Nonacyclo (9. 10.1. 14 and 7 . 03 and 8 . 02, 10.012, and 21 . 113 and 20 . 014 and 19 . 115 and 19)-5-pen ******** or its derivative can be raised.

[0008] The copolymerization polymer which the homopolymer which can raise ethylene and a propylene, 1-butene, 1-pentene, a 4-methyl-pentene, a 3-methyl-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc., and consists of these 1 component as a component of the polyolefine which makes an annular olefin component contain, for example also turns into from two or more components is sufficient. Although there is a structural unit originating in an ethylene component in the annular polyolefine copolymer which made the annular olefin component contain and the structural unit which originates in the 50-80 mol domain of %, and an annular polyolefine component preferably is from 1 mol % addition 40-95 mol%, usually, 5-60 mol%, the 20-50 mol domain of % is suitable, and the structural unit originating in olefin components, such as an ethylene component, is arranged at random, and forms the annular polyolefine copolymer preferably.

[0009] Moreover, the impact strength which the aforementioned annular polyolefine copolymer has can compensate small the fault that a moldability is bad, by excelling in shock resistance and using the polyolefine system resin with a sufficient moldability by making the aforementioned annular polyolefine copolymer intervene between polyolefine system resins.

[0010] Polyolefin resin, such as a resin of the simple substance of the resin which added the ethylene-alpha olefin copolymer or the propylene-alpha olefin copolymer, an ethylene-alpha olefin copolymer, or a propylene-alpha olefin copolymer, or two or more kinds of such mixture can be used for the general polyolefin resin as a polyolefine system resin between which this aforementioned annular polyolefine copolymer is made to be placed as an interlayer, i.e., a polyethylene resin, polypropylene resin, a poly-methyl pentene resin, a polybutene resin, an ethylene-vinyl acetate copolymer, etc.

[0011] The concrete configuration in the case of using the multilayer-structure object of this invention can take arbitrary arrangement, as long as the polyolefine (B) which has an annular olefin is made to intervene between polyolefine system resins (A), for example, it takes the configuration of the following (b).

(b) Three laminations of A/B/A [0012] In the lamination of the aforementioned (b) when the adhesive property between layers is scarce An adhesive resin (C) can also be intervened between resin layers. as an adhesive resin in this case An acid denaturation olefine resin, For example, the polyethylene by which graft denaturation was carried out with an ethylene system unsaturated carboxylic acid or its anhydrides, such as a maleic anhydride, an acrylic acid, a methacrylic acid, and itaconic acid anhydride Adhesive resins, such as polypropylene and an ethylene-alpha olefin copolymer, or 99-70 mols % of the ethylene of ethylene contents, At least one sort of copolymers chosen out of the metal salt of the copolymer with an unsaturation monocarboxylic acid and the copolymer with an unsaturation monocarboxylic acid and the copolymer with unsaturation monocarboxylic-acid ester can be made to intervene. In this case, the configuration of the following (b) is taken as opposed to the polyolefine (B) which has an annular olefin.

(b) Five laminations of A/C/B/C/A [0013] When gas barrier nature, such as oxygen, is

demanded in addition to shock resistance, thermal resistance, and steam barrier nature, the configuration of the following (c) - (h) is taken as opposed to a gas barrier nature resin (D).

(c) As a gas barrier nature resin (D) of the four lamination aforementioned [4 lamination (**)A/B/A/D of 5 lamination (**)A/D/B/A of 4 lamination (**)A/B/D/B/A / 4 lamination (**)A/B/D/A/D / of 5 lamination (**)D/A/B/A] (**) - (**) of A/B/D/A The copolymer which consists of **, polybasic acid, and polyhydric alcohol Or the copolymer which contains other polybasic acid and other polyhydric-alcohol components in polybasic acid and polyhydric alcohol as a comonomer component, respectively, An ethylene content a 25-60 mol ethylene [which is %]-vinyl acetate copolymer The copolymer from which the degree of saponification saponifies to 96% or more, and is obtained, the gay polyamide which the number of the amide groups per 100 carbon numbers contains in the 3-30 domains, a ****** amide, or its blend resin can use it suitably. Moreover, when the adhesive property between layers is scarce, an adhesive resin can also be intervened between resin layers and adhesive resins, such as polyethylene by which graft denaturation was carried out as an adhesive resin in this case with an ethylene system unsaturated carboxylic acid or its anhydrides, such as an acid denaturation olefine resin, for example, a maleic anhydride, an acrylic acid, a methacrylic acid, and itaconic acid anhydride, polypropylene, and an ethylene-alpha olefin copolymer, can be made to intervene in the above mentioned lamination.

[0014] The dampproof multilayer-structure object of this invention can also intervene a scrap resin, and, specifically, the lamination of the following (i) and (j) is raised to a scrap resin layer (E).

(i) In the configuration which contains a scrap resin layer in 5 lamination pan of 4 lamination (j)A/E/B/E/A of A/B/E/A, the hindrance does not have the thing with a configuration of that the above mentioned gas barrier nature resin layer is included to combine in any way, either. Moreover, when the adhesive property between layers is scarce, the adhesive resin described above between resin layers can also be intervened.

[0015] As a concrete lamination in the case of carrying out the bag making of the multilayer-structure object of this invention by heat sealing etc., the resin layer with a heat deflection temperature higher than a sealant layer, for example, a polyester system resin, a polyamide system resin, a polycarbonate system resin, a polyacrylonitrile system resin, etc. can use it good as a base-material layer (F). Even if the aforementioned base-material layer is the configuration of a biaxially oriented film as a base material by the general extrusion laminating method (a dry laminate, wet lamination), it does not interfere, for example, in the case of a polyester system resin, a biaxial stretching is carried out four to 6 times in four to 6 times, and longitudinal direction the lengthwise one after molding, and the biaxial-stretching polyester film which carried out biaxial-stretching post heating fixation is used preferably. Or even if a base-material layer is co-extrusion, it does not interfere, and further, even if it uses the base-material layer by which vacuum evaporationo was carried out with the metal etc., it does not interfere at all. Moreover, the polyolefine system resin in a sealant lamination can use polyolefin resin, such as a resin, or these blend resins of a simple substance of the resin which added the ethylene-alpha olefin copolymer or the propylene-alpha olefin copolymer, an ethylene-alpha olefin copolymer, or a propylene-alpha olefin copolymer etc. for general polyolefin resin, i.e., a polyethylene resin, polypropylene resin, a poly-methyl pentene

resin, a polybutene resin, an ethylene-vinyl acetate copolymer, etc., and the lamination of the following (**) is specifically raised to a base-material layer (F).

(**) In the lamination of F/A/B / the A aforementioned (**), when the adhesive property between layers is scarce, the hindrance does not have the thing with a configuration of that the scrap layer containing the gas barrier nature resin layer which could also intervene and described above further the adhesive resin described above between resin layers constituted and described above in addition is included to combine in any way, either.

[0016] The dampproof multilayer-extrusion structure excellent in the shock resistance in this invention has a variation which described above the polyolefine which has 5-60 mols % of annular olefin components on the basis of three laminations made to be placed between polyolefin resin, and even if the lamination is symmetrical and it is unsymmetrical, it does not interfere.

[0017]

[Operation] In this invention, offer of the dampproof multilayer-extrusion structure excellent in shock resistance is enabled by making the polyolefin resin layer which has 5-60 mols % of annular olefin components intervene between polyolefine system resin layers.

[0018]

[Example] The example and its example of a comparison of this invention are shown below.

Using the multilayer-extrusion blow molding machine which has the screw extruder of 1> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as a polyethylene resin and an interlayer resin, and three laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an internal layer.

[0019] Using the multilayer-extrusion blow molding machine which has the screw extruder of 2> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as polypropylene resin and an interlayer resin, and three laminations of polypropylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an internal layer.

[0020] Using the multilayer-extrusion blow molding machine which has the screw extruder of 3> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 20 mol % and ethylene component; 80 mol %) resin was fabricated as a polyethylene resin and an interlayer resin, and three laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an internal layer.

[0021] Using the multilayer-extrusion making machine which has the screw extruder of 4> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as a polyethylene resin and an interlayer resin, the sheet with three laminations [of a polyethylene resin] and a mean thickness of 2mm was fabricated as an internal layer, and 500 micrometers of drum section average wall thicknesss and the cup of 100ml of content volume were further fabricated with the vacuum forming.

[0022] Using the multilayer extension blow molding machine which has the screw extruder of 5> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as polypropylene resin and an interlayer resin, and one 4.70 times the field scale factor [three laminations of polypropylene resin, 550 micrometers of drum section average wall thicknesss, a 2.0 times as many vertical draw magnification as this a 2.35 times

[0023] The multilayer-extrusion blow molding machine which has the screw extruder of 6> 6 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer Six laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer (innermost layer).

[0024] The multilayer-extrusion blow molding machine which has the screw extruder of 7> 7 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer Seven laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 7th layer (innermost layer).

[0025] The multilayer-extrusion blow molding machine which has the screw extruder of 8> 5 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 3rd layer as a polyethylene resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier resin of the 5th layer (innermost layer) Five laminations of the copolymer from which an ethylene content saponifies a 25 mol ethylene [which is %]-vinyl acetate copolymer to the 96% of the degrees of saponification, and is obtained, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated.

[0026] The multilayer-extrusion blow molding machine which has the screw extruder of 9> 8 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As

the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer As a polyethylene resin and a layer [7th] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of an octavus layer (innermost layer) Eight laminations of the copolymer from which an ethylene content saponifies a 25 mol ethylene [which is %]-vinyl acetate copolymer to the 96% of the degrees of saponification, and is obtained, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated.

[0027] The multilayer-extrusion blow molding machine which has the screw extruder of 10> 5 < examples is used. as a gas barrier resin of the 1st layer (the outermost layer) An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [2nd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer The annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as a polyethylene resin and the 4th layer, and five laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the 5th layer (innermost layer).

[0028] The multilayer-extrusion blow molding machine which has the screw extruder of 11> 5 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin An annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, The maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer was fabricated as a layer [4th] adhesives layer, and five laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the 5th layer (innermost layer).

[0029] The multilayer-extrusion blow molding machine which has the screw extruder of 12> 4 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] scrap layer Four laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as a polyethylene resin, the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio, and the 4th layer (innermost layer).

[0030] The multilayer-extrusion blow molding machine which has the screw extruder of 13> 7 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer resin, an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, As a layer [3rd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer The copolymer from which an ethylene content

saponifies a 25 mol ethylene [which is %]-vinyl acetate copolymer to the 96% of the degrees of saponification, and is obtained, As a layer [5th] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [6th] scrap layer Seven laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as a polyethylene resin, the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio, and the 7th layer (innermost layer).

[0031] The multilayer-extrusion blow molding machine which has the screw extruder of 14> 7 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 5th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [6th] adhesives layer Seven laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 7th layer (innermost layer).

[0032] The multilayer-extrusion blow molding machine which has the screw extruder of 15> 8 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 5th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [6th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [7th] scrap layer Eight laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as a polyethylene resin, the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio, and an octavus layer (innermost layer).

[0033] The multilayer-extrusion making machine which has the screw extruder of 16> 4 < examples is used. as a base-material layer (the outermost layer) As a polyethylene-terephthalate resin and the 2nd layer resin, as a polyethylene resin and the 3rd layer resin An annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, As the 4th layer (innermost layer) resin, the film with four laminations [of a polyethylene resin] and a mean thickness of 250 micrometers was fabricated, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0034] <Example 17> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin

fabricated using the multilayer-extrusion making machine which has three screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 3rd layer resin The cladding and (lamination side fabricated the film with a base-material layer, and a thickness [) between the 1st layer and mean thickness] of 250 micrometers for the film of three laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0035] <Example 18> The biaxial-stretching polyethylene-terephthalate resin configuration film by which aluminum vacuum evaporationo was beforehand carried out to the base-material layer, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has three screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 3rd layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of three laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0036] <Example 19> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has four screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and the 4th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of four laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0037] <Example 20> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has five screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 5th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of five laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0038] <Example 21> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has six screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride

denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [5th] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and the 6th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of six laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0039] <Example 22> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has six screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of six laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0040] <Example 23> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, Seven screw extruders as the 1st layer resin fabricated using the existing multilayer-extrusion making machine As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [6th] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and the 7th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of seven laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0041] <Example 24> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has seven screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-

anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin

EFFECT OF THE INVENTION

[Effect of the invention] According to the technique of this invention, in points, such as physical properties and a moldability, it is good by making the polyolefin resin layer which has 5-60 mols % of annular olefin components between polyolefine system resin layers intervene, excels in shock resistance, and is enabled to obtain the multilayer container excellent in the dampproofing using the multilayer-extrusion structure and it excellent in dampproofing from the further conventional polyolefine system resin.

MEANS

[The means for solving a technical problem] this invention is the dampproof multilayer container fabricated using the dampproof multilayer-extrusion structure and it excellent in the shock resistance which considers the resin configuration of at least three layers as a basic configuration which made the polyolefin resin layer which has 5-60 mols % of annular olefin components intervene between polyolefine system resin layers.

[0006] Hereafter, it explains still in detail. The important characteristic feature in the dampproof multilayer-extrusion structure excellent in the shock resistance by this invention is that it uses the polyolefine which has 5-60 mols % of annular olefin components as an interlayer. the polyolefine which has this annular olefin ****** -- hydrogen and carbon **** -- **** -- the becoming resin of a polyolefine system -- it is -- in addition -- and the cyclic structure which checks the crystal structure to the principal chain skeleton or a side chain and an umbrella -- although factors, such as high structure, should just exist, the resin "an annular polyolefine copolymer" of the polyolefine system which has an annular polyolefine component is preferably used for the chief examiner skeleton

[0007] As an annular olefin component, for example Bicyclo (2.2.1) hept-2-**** or its derivative, Tetracyclo (4. 4.0. 12 and 5 . 17, 10)-3-dodecen or its derivative, Hexa cyclo (6. 6.1.13, 6.110, 13.02, 7. 09, 14)-4-heptadecene or its derivative, Octacyclo (8. 8.0. 12 and 9 . 14 and 7 . 111 and 10 . 113 and 16 . 03 and 8 . 012 and 17)-5-******** or its derivative, ****** cyclo (6. 6.1. 13 and 6 . 02 and 7 . 09, 14)-4-hexa decene or its derivative, ****** cyclo (6. 5.1. 13 and 6 . 02 and 7 . 09, 13)-4-pentadecene or its derivative, Heptacyclo (8. 7.0. 12 and 9 . 14 and 7 . 111 and 16 . 03 and 8 . 012 and 16)-5-********** or its derivative, Tricyclo (4. 4.0. 12 and 5)-3-undecene or its derivative, Tricyclo (4. 3.0. 12 and 5)-3-decene or its derivative, Cyclo [****** / -4] (6. 5.1.13, 6. 02 and 7 . 09, 13), 10-****** deca diene, or its derivative, ****** cyclo (4. 7.0.12, 5.08, 13. 19, 12)-3-pentadecene or its derivative, Heptacyclo (7. 8.0. 13 and 6 . 02 and 7 . 110 and 17 . 011 and 16 . 112 and 15)-4-ray ****** or its derivative, Nonacyclo (9. 10.1. 14 and 7 . 03 and 8 . 02, 10.012, and 21 . 113 and 20 . 014 and 19 . 115 and 19)-5-pen ******** or its derivative can be raised.

[0008] The copolymerization polymer which the homopolymer which can raise ethylene and a propylene, 1-butene, 1-pentene, a 4-methyl-pentene, a 3-methyl-pentene, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, etc., and consists of these 1 component as a

component of the polyolefine which makes an annular olefin component contain, for example also turns into from two or more components is sufficient. Although there is a structural unit originating in an ethylene component in the annular polyolefine copolymer which made the annular olefin component contain and the structural unit which originates in the 50-80 mol domain of %, and an annular polyolefine component preferably is from 1 mol % addition 40-95 mol%, usually, 5-60 mol%, the 20-50 mol domain of % is suitable, and the structural unit originating in olefin components, such as an ethylene component, is arranged at random, and forms the annular polyolefine copolymer preferably.

[0009] Moreover, the impact strength which the aforementioned annular polyolefine copolymer has can compensate small the fault that a moldability is bad, by excelling in shock resistance and using the polyolefine system resin with a sufficient moldability by making the aforementioned annular polyolefine copolymer intervene between polyolefine system resins.

[0010] Polyolefin resin, such as a resin of the simple substance of the resin which added the ethylene-alpha olefin copolymer or the propylene-alpha olefin copolymer, an ethylene-alpha olefin copolymer, or a propylene-alpha olefin copolymer, or two or more kinds of such mixture can be used for the general polyolefin resin as a polyolefine system resin between which this aforementioned annular polyolefine copolymer is made to be placed as an interlayer, i.e., a polyethylene resin, polypropylene resin, a poly-methyl pentene resin, a polybutene resin, an ethylene-vinyl acetate copolymer, etc.

[0011] The concrete configuration in the case of using the multilayer-structure object of this invention can take arbitrary arrangement, as long as the polyolefine (B) which has an annular olefin is made to intervene between polyolefine system resins (A), for example, it takes the configuration of the following (b).

(b) Three laminations of A/B/A [0012] In the lamination of the aforementioned (b) when the adhesive property between layers is scarce An adhesive resin (C) can also be intervened between resin layers. as an adhesive resin in this case An acid denaturation olefine resin, For example, the polyethylene by which graft denaturation was carried out with an ethylene system unsaturated carboxylic acid or its anhydrides, such as a maleic anhydride, an acrylic acid, a methacrylic acid, and itaconic acid anhydride Adhesive resins, such as polypropylene and an ethylene-alpha olefin copolymer, or 99-70 mols % of the ethylene of ethylene contents, At least one sort of copolymers chosen out of the metal salt of the copolymer with an unsaturation monocarboxylic acid and the copolymer with an unsaturation monocarboxylic acid and the copolymer with unsaturation monocarboxylic-acid ester can be made to intervene. In this case, the configuration of the following (b) is taken as opposed to the polyolefine (B) which has an annular olefin.

(b) Five laminations of A/C/B/C/A [0013] When gas barrier nature, such as oxygen, is demanded in addition to shock resistance, thermal resistance, and steam barrier nature, the configuration of the following (c) - (h) is taken as opposed to a gas barrier nature resin (D).

(c) As a gas barrier nature resin (D) of the four lamination aforementioned [4 lamination (**)A/B/A/D of 5 lamination (**)A/D/B/A of 4 lamination (**)A/B/D/B/A / 4 lamination (**)A/B/D/A/D / of 5 lamination (**)D/A/B/A] (**) - (**) of A/B/D/A The copolymer which consists of **, polybasic acid, and polyhydric alcohol Or the copolymer which contains other polybasic acid and other polyhydric-alcohol components in polybasic acid

and polyhydric alcohol as a comonomer component, respectively, An ethylene content a 25-60 mol ethylene [which is %]-vinyl acetate copolymer The copolymer from which the degree of saponification saponifies to 96% or more, and is obtained, the gay polyamide which the number of the amide groups per 100 carbon numbers contains in the 3-30 domains, a ****** amide, or its blend resin can use it suitably. Moreover, when the adhesive property between layers is scarce, an adhesive resin can also be intervened between resin layers and adhesive resins, such as polyethylene by which graft denaturation was carried out as an adhesive resin in this case with an ethylene system unsaturated carboxylic acid or its anhydrides, such as an acid denaturation olefine resin, for example, a maleic anhydride, an acrylic acid, a methacrylic acid, and itaconic acid anhydride, polypropylene, and an ethylene-alpha olefin copolymer, can be made to intervene in the above mentioned lamination.

[0014] The dampproof multilayer-structure object of this invention can also intervene a scrap resin, and, specifically, the lamination of the following (i) and (j) is raised to a scrap resin layer (E).

(i) In the configuration which contains a scrap resin layer in 5 lamination pan of 4 lamination (j)A/E/B/E/A of A/B/E/A, the hindrance does not have the thing with a configuration of that the above mentioned gas barrier nature resin layer is included to combine in any way, either. Moreover, when the adhesive property between layers is scarce, the adhesive resin described above between resin layers can also be intervened.

[0015] As a concrete lamination in the case of carrying out the bag making of the multilayer-structure object of this invention by heat sealing etc., the resin layer with a heat deflection temperature higher than a sealant layer, for example, a polyester system resin, a polyamide system resin, a polycarbonate system resin, a polyacrylonitrile system resin, etc. can use it good as a base-material layer (F). Even if the aforementioned base-material layer is the configuration of a biaxially oriented film as a base material by the general extrusion laminating method (a dry laminate, wet lamination), it does not interfere, for example, in the case of a polyester system resin, a biaxial stretching is carried out four to 6 times in four to 6 times, and longitudinal direction the lengthwise one after molding, and the biaxial-stretching polyester film which carried out biaxial-stretching post heating fixation is used preferably. Or even if a base-material layer is co-extrusion, it does not interfere, and further, even if it uses the base-material layer by which vacuum evaporationo was carried out with the metal etc., it does not interfere at all. Moreover, the polyolefine system resin in a sealant lamination can use polyolefin resin, such as a resin, or these blend resins of a simple substance of the resin which added the ethylene-alpha olefin copolymer or the propylene-alpha olefin copolymer, an ethylene-alpha olefin copolymer, or a propylene-alpha olefin copolymer etc. for general polyolefin resin, i.e., a polyethylene resin, polypropylene resin, a poly-methyl pentene resin, a polybutene resin, an ethylene-vinyl acetate copolymer, etc., and the lamination of the following (**) is specifically raised to a base-material layer (F).

(**) In the lamination of F/A/B / the A aforementioned (**), when the adhesive property between layers is scarce, the hindrance does not have the thing with a configuration of that the scrap layer containing the gas barrier nature resin layer which could also intervene and described above further the adhesive resin described above between resin layers constituted and described above in addition is included to combine in any way, either.

[0016] The dampproof multilayer-extrusion structure excellent in the shock resistance in this invention has a variation which described above the polyolefine which has 5-60 mols % of annular olefin components on the basis of three laminations made to be placed between polyolefin resin, and even if the lamination is symmetrical and it is unsymmetrical, it does not interfere.

EXAMPLE

[Example] The example and its example of a comparison of this invention are shown below.

Using the multilayer-extrusion blow molding machine which has the screw extruder of 1> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as a polyethylene resin and an interlayer resin, and three laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an internal layer.

[0019] Using the multilayer-extrusion blow molding machine which has the screw extruder of 2> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as polypropylene resin and an interlayer resin, and three laminations of polypropylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an internal layer.

[0020] Using the multilayer-extrusion blow molding machine which has the screw extruder of 3> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 20 mol % and ethylene component; 80 mol %) resin was fabricated as a polyethylene resin and an interlayer resin, and three laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an internal layer.

[0021] Using the multilayer-extrusion making machine which has the screw extruder of 4> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as a polyethylene resin and an interlayer resin, the sheet with three laminations [of a polyethylene resin] and a mean thickness of 2mm was fabricated as an internal layer, and 500 micrometers of drum section average wall thicknesss and the cup of 100ml of content volume were further fabricated with the vacuum forming.

[0022] Using the multilayer extension blow molding machine which has the screw extruder of 5> 3 < examples, as an outer layer, the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as polypropylene resin and an interlayer resin, and one 4.70 times the field scale factor [three laminations of polypropylene resin, 550 micrometers of drum section average wall thicknesss, a 2.0 times as many vertical draw magnification as this a 2.35 times

[0023] The multilayer-extrusion blow molding machine which has the screw extruder of 6> 6 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As

the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer Six laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer (innermost layer).

[0024] The multilayer-extrusion blow molding machine which has the screw extruder of 7> 7 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer Seven laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 7th layer (innermost layer).

[0025] The multilayer-extrusion blow molding machine which has the screw extruder of 8> 5 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 3rd layer as a polyethylene resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier resin of the 5th layer (innermost layer) Five laminations of the copolymer from which an ethylene content saponifies a 25 mol ethylene [which is %]-vinyl acetate copolymer to the 96% of the degrees of saponification, and is obtained, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated.

[0026] The multilayer-extrusion blow molding machine which has the screw extruder of 9> 8 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer As a polyethylene resin and a layer [7th] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of an octavus layer (innermost layer) Eight laminations of the copolymer from which an ethylene content saponifies a 25 mol ethylene [which is %]-vinyl acetate copolymer to the 96% of the degrees of saponification, and is obtained, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content

volume were fabricated.

[0027] The multilayer-extrusion blow molding machine which has the screw extruder of 10> 5 < examples is used. as a gas barrier resin of the 1st layer (the outermost layer) An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [2nd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer The annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin was fabricated as a polyethylene resin and the 4th layer, and five laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the 5th layer (innermost layer).

[0028] The multilayer-extrusion blow molding machine which has the screw extruder of 11> 5 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin An annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, The maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer was fabricated as a layer [4th] adhesives layer, and five laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the 5th layer (innermost layer).

[0029] The multilayer-extrusion blow molding machine which has the screw extruder of 12> 4 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] scrap layer Four laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as a polyethylene resin, the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio, and the 4th layer (innermost layer).

[0030] The multilayer-extrusion blow molding machine which has the screw extruder of 13> 7 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and the 2nd layer resin, an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, As a layer [3rd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer The copolymer from which an ethylene content saponifies a 25 mol ethylene [which is %]-vinyl acetate copolymer to the 96% of the degrees of saponification, and is obtained, As a layer [5th] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [6th] scrap layer Seven laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as a polyethylene resin, the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio, and the 7th layer (innermost layer).

[0031] The multilayer-extrusion blow molding machine which has the screw extruder of 14> 7 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of

ethylene and an alpha olefin copolymer, and the 3rd layer As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 5th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [6th] adhesives layer Seven laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 7th layer (innermost layer).

[0032] The multilayer-extrusion blow molding machine which has the screw extruder of 15> 8 < examples is used. as the 1st layer (the outermost layer) As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 5th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [6th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [7th] scrap layer Eight laminations of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated as a polyethylene resin, the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio, and an octavus layer (innermost layer).

[0033] The multilayer-extrusion making machine which has the screw extruder of 16> 4 < examples is used. as a base-material layer (the outermost layer) As a polyethylene-terephthalate resin and the 2nd layer resin, as a polyethylene resin and the 3rd layer resin An annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, As the 4th layer (innermost layer) resin, the film with four laminations [of a polyethylene resin] and a mean thickness of 250 micrometers was fabricated, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0034] <Example 17> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has three screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 3rd layer resin The cladding and (lamination side fabricated the film with a base-material layer, and a thickness [) between the 1st layer and mean thickness] of 250 micrometers for the film of three laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0035] <Example 18> The biaxial-stretching polyethylene-terephthalate resin configuration film by which aluminum vacuum evaporationo was beforehand carried out to the base-material layer, As the 1st layer resin fabricated using the multilayer-extrusion

making machine which has three screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and the 3rd layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of three laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0036] <Example 19> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has four screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and the 4th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of four laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0037] <Example 20> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has five screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 5th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of five laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0038] <Example 21> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has six screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [5th] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and the 6th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of six laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0039] <Example 22> The base-material layer of the polyethylene-terephthalate resin

configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has six screw extruders As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 6th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of six laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0040] <Example 23> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, Seven screw extruders as the 1st layer resin fabricated using the existing multilayer-extrusion making machine As a polyethylene resin and the 2nd layer resin, as an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [3rd] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 4th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [5th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [6th] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and the 7th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of seven laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0041] <Example 24> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has seven screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 5th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [6th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 7th layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of seven laminations of a polyethylene resin by the dry-laminate method, and the bag making of

the pouch of 200ml of content volume was further carried out by heat sealing.

[0042] <Example 25> The base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, As the 1st layer resin fabricated using the multilayer-extrusion making machine which has eight screw extruders As a polyethylene resin and a layer [2nd] adhesives layer, as the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and the 3rd layer resin As an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin and a layer [4th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a gas barrier nature resin of the 5th layer An ethylene content a 25 mol ethylene [which is %]-vinyl acetate copolymer as the copolymer which saponifies to the 96% of the degrees of saponification, and is obtained, and a layer [6th] adhesives layer As the maleic-anhydride denaturation object of ethylene and an alpha olefin copolymer, and a layer [7th] scrap layer As a polyethylene resin, and the resin which mixed the scrap material of the multilayer-structure object which consists of this example by 50:50-fold quantitative ratio and an octavus layer resin The film with a cladding (lamination side for a base-material layer and the 1st layer) and a mean thickness of 250 micrometers was fabricated for the film of eight laminations of a polyethylene resin by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0043] The monolayer configuration of a polyethylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated using the blow molding machine which has the screw extruder of 1> 1 example of < comparison.

[0044] The monolayer configuration of polypropylene resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated using the blow molding machine which has the screw extruder of 2> 1 example of < comparison.

[0045] The monolayer configuration of an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, 750 micrometers of drum section average wall thicknesss, and the bottle of 800ml of content volume were fabricated using the blow molding machine which has the screw extruder of 3> 1 example of < comparison.

[0046] Using the extruding press machine which has the screw extruder of 4> 1 example of < comparison, the sheet with a monolayer configuration [of polypropylene resin] and a mean thickness of 2mm was fabricated, and 500 micrometers of drum section average wall thicknesss and the cup of 100ml of content volume were further fabricated with the vacuum forming.

[0047] Using the extruding press machine which has the screw extruder of 5> 1 example of < comparison, the sheet with a monolayer configuration [of an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin] and a mean thickness of 2mm was fabricated, and 500 micrometers of drum section average wall thicknesss and the cup of 100ml of content volume were further fabricated with the vacuum forming.

[0048] One 4.70 times the field scale factor [the monolayer configuration of polypropylene resin, 550 micrometers of drum section average wall thicknesss, a 2.0

times as many vertical draw magnification as this, a 2.35 times as many horizontal draw magnification as this, and] of this, and the surface-area 2 and the bottle of 500ml of content volume of 0.050m were fabricated using the extension blow molding machine which has the screw extruder of 6> 1 example of < comparison.

[0049] One 4.70 times the field scale factor [the monolayer configuration of an annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin, 550 micrometers of drum section average wall thicknesss, a 2.0 times as many vertical draw magnification as this, a 2.35 times as many horizontal draw magnification as this, and] of this, and the surface-area 2 and the bottle of 500ml of content volume of 0.050m were fabricated using the extension blow molding machine which has the screw extruder of 7> 1 example of < comparison.

[0050] Using the multilayer-extrusion making machine which has the screw extruder of 8> 2 examples of < comparison, the polyethylene-terephthalate resin was fabricated as a base-material layer (outer layer), the film with a two-layer configuration [of polypropylene resin] and a mean thickness of 250 micrometers was fabricated as an internal layer, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0051] <Example 9 of a comparison> The film with a cladding and a mean thickness of 250 micrometers was fabricated for the monolayer film of the annular polyolefine copolymer (annular olefin component; 50 mol % and ethylene component; 50 mol %) resin fabricated using the multilayer-extrusion making machine which has the base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, and one screw extruder by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0052] <Example 10 of a comparison> The film with a cladding and a mean thickness of 250 micrometers was fabricated for the film of a polyethylene resin fabricated using the multilayer-extrusion making machine which has the base-material layer of the polyethylene-terephthalate resin configuration film by which the biaxial stretching was carried out, and one screw extruder by the dry-laminate method, and the bag making of the pouch of 200ml of content volume was further carried out by heat sealing.

[0053] The above result is shown in (Table 1) and the (Table 2). (The evaluation technique) About the fall impact strength, ten containers were filled up with water to full of water, and the number of crack books at the time of making 5 degrees C carry out free fall 10 times on concrete in the state of [height / of 1m] **** after a 12 hour store was measured. About a moisture vapor transmission, it is JIS. Moisture-vapor-transmission measurement based on Z0222 was performed.

[0054]

[Table 1]

	落下衝撃強度 (破損個数)	透湿度 (mg／pkg－30days)
実施例1	0	205
実施例2	0	198
実施例3	0	201
実施例4	0	146
実施例5	0	87
実施例6	0	195
実施例7	0	176
実施例8	0	202
実施例9	0	199
実施例10	0	203
実施例11	0	209
実施例12	0	214
実施例13	0	197
実施例14	0	205
実施例15	0	192
実施例16	0	479
実施例17	0	499
実施例18	0	101
実施例19	0	498
実施例20	0	571
実施例21	0	582
実施例22	0	573
実施例23	0	475
実施例24	0	596
実施例25	0	587

[0055] (Table 1) shows the physical properties of the container obtained in each example.

[0056]

[Table 2]

	落下衝撃強度 (破損個数)	透湿度 (mg／pkg－30days)
比較例1	0	610
比較例2	0	650
比較例3	10	200
比較例4	0	470
比較例5	10	151
比較例6	0	385
比較例7	10	179
比較例8	0	1910
比較例9		410
比較例10		1830

[0057] (Table 2) shows the physical properties of the container obtained in each example of a comparison.

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(71)出願人　000003193
凸版印刷株式会社
東京都台東区台東１丁目５番１号

(72)発明者　福島　英夫
東京都台東区台東一丁目５番１号　凸版印刷株式会社内

(72)発明者　寺内　祐介
東京都台東区台東一丁目５番１号　凸版印刷株式会社内

(72)発明者　鹿島　浩人
東京都台東区台東一丁目５番１号　凸版印刷株式会社内

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(54)【発明の名称】　防湿性多層押出構造物およびそれを用いた防湿性多層容器

(57)【要約】

【目的】防湿包装用の構造物において、耐衝撃性に優れ、更に従来のポリプロピレン等のポリオレフィン系の樹脂からなる構造物よりも防湿性に優れた多層押出構造物および多層容器、又は防湿高酸素バリア性に優れた多層押出構造物および多層容器を提供する。

【構成】ポリオレフィン系樹脂層の間に、環状オレフィン成分５～６０モル%を有するポリオレフィン樹脂層を介在させた、少なくとも３層の樹脂構成を基本構成とする耐衝撃性に優れた防湿性多層押出構造物およびそれを用いて成形した防湿性多層容器である。

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【特許請求の範囲】

【請求項１】ポリオレフィン系樹脂層の間に、環状オレフィン成分５～６０モル％を有するポリオレフィン樹脂層を介在させたことを特徴とする、少なくとも３層の樹脂構成からなる耐衝撃性に優れた防湿性多層押出構造物。

【請求項２】前記ポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項１記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項３】請求項１記載の樹脂構成において、ポリオレフィン系樹脂層の間に接着性樹脂層を、少なくとも１層有することを特徴とする耐衝撃性に優れた防湿性多層押出構造物。

【請求項４】前記ポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項３記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項５】請求項１記載の樹脂構成において、ガスバリア性樹脂層を少なくとも１層有することを特徴とする耐衝撃性に優れた防湿性多層押出構造物。

【請求項６】前記ポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項５記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項７】請求項５記載の樹脂構成において、最外層となる樹脂層と最内層となる樹脂層の間に接着性樹脂層を、少なくとも１層有することを特徴とする耐衝撃性に優れた防湿性多層押出構造物。

【請求項８】前記ポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項７記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項９】シーラント層として、請求項１記載の耐衝撃性に優れた防湿性多層押出構造物からなる層構成、外層である基材層として、シーラント層構成中の最内層樹脂層であるポリオレフィン系樹脂層より熱変形温度の高い樹脂層を有することを特徴とする、少なくとも４層の樹脂構成からなる耐衝撃性に優れた防湿性多層押出構造物。

【請求項１０】前記シーラント層構成中のポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項９記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項１１】請求項９記載の樹脂構成において、各樹脂層の間に接着性樹脂層を、少なくとも１層有することを特徴とする耐衝撃性に優れた防湿性多層押出構造物。

【請求項１２】前記シーラント層構成中のポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項１１記載の耐衝撃性に優れた防湿性多層押出構造物。

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【請求項１３】請求項９記載の樹脂構成において、シーラント層構成中のポリオレフィン系樹脂層の間に、ガスバリア性樹脂層を、少なくとも１層有することを特徴とする耐衝撃性に優れた防湿性多層押出構造物。

【請求項１４】前記シーラント層構成中のポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項１３記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項１５】請求項１３記載の樹脂構成において、各樹脂層の間に接着性樹脂層を、少なくとも１層有することを特徴とする耐衝撃性に優れた防湿性多層押出構造物。

【請求項１６】前記シーラント層構成中のポリオレフィン系樹脂層の間に、前記防湿性多層押出構造物のリサイクル材料を含有する層を、少なくとも１層有することを特徴とする請求項１５記載の耐衝撃性に優れた防湿性多層押出構造物。

【請求項１７】請求項１乃至請求項１６に記載の防湿性多層押出構造物において、多層シート成形品であることを特徴とする、耐衝撃性に優れた防湿性多層押出構造物。

【請求項１８】請求項１乃至請求項８に記載の防湿性多層押出構造物であって、多層シートの真空成形又は圧空成形、あるいは真空圧空成形方法を用いて成形されたことを特徴とする、耐衝撃性に優れた防湿性多層容器。

【請求項１９】請求項１乃至請求項８に記載の防湿性多層押出構造物であって、該防湿性多層押出構造物を多層ブロー成形方法を用いて成形されたことを特徴とする、耐衝撃性に優れた防湿性多層容器。

【請求項２０】請求項１乃至請求項８に記載の防湿性多層押出構造物であって、該防湿性多層押出構造物を多層延伸ブロー成形方法を用いて成形されたことを特徴とする、耐衝撃性に優れた防湿性多層容器。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は、水蒸気バリアが良好かつ、耐衝撃性に優れた防湿性多層押出構造物および、防湿性高酸素バリア多層押出構造物に関するものであり、さらに詳しくは、多層押出ブロー成形法、多層共押出法、多層延伸ブロー成形法、ラミネート法、更には、多層シートより真空又は圧空法で成形され、容器、及び袋等に使用することができる防湿性多層押出構造物に関する。

【０００２】

【従来の技術】従来、防湿包装用の材質として、ポリプロピレン等のポリオレフィン系の樹脂が、価格、物性、

及び成形性などの点において良好であり、多く用いられている。しかし、例えばポリプロピレンの場合、水蒸気バリア性は透湿係数０．３ｇ・ｍｍ／ｍ^2・２４ｈｒ（ＡＳＴＭＦ１２４９）であり、前記以上の水蒸気バリア性が要求される内容物においては、ポリプロピレンで成形した包装の他に内袋、あるいは乾燥剤（水蒸気吸収剤）等を併用するなどしている。この形態において、内袋を用いることにより過剰包装となり、使用時の簡便性が乏しい、廃棄物が多く出るなどの問題があり、あるいは乾燥剤を用いることによる内容物との混同（例えば、錠剤と間違えて誤飲してしまう等）、乾燥剤の寿命等の問題があった。

【０００３】また、ポリプロピレンより水蒸気バリア性の優れた樹脂として、結晶化度が２０％以下である様に環状オレフィン成分５～６０モル％を含有させたポリオレフィンがある。ただし、前記ポリオレフィン単独では成形性が悪く、更に耐衝撃性が乏しく使用に耐えないものにしかならなかった。

【０００４】

【発明が解決しようとする課題】本発明は、上記の様な従来技術の問題点を解決する為になされたものであり、防湿包装用の構造物において、耐衝撃性に優れ、更に従来のポリプロピレン等のポリオレフィン系の樹脂からなる構造物よりも防湿性に優れた多層押出構造物および多層容器、又は防湿高酸素バリア性に優れた多層押出構造物および多層容器を提供するものである。

【０００５】

【課題を解決するための手段】本発明は、ポリオレフィン系樹脂層の間に、環状オレフィン成分５～６０モル％を有するポリオレフィン樹脂層を介在させた、少なくとも３層の樹脂構成を基本構成とする耐衝撃性に優れた防湿性多層押出構造物およびそれを用いて成形した防湿性多層容器である。

【０００６】以下、さらに詳しく説明する。本発明による耐衝撃性に優れた防湿性多層押出構造物における重要な特徴は、中間層として環状オレフィン成分５～６０モル％を有するポリオレフィンを使用する点にある。この環状オレフィンを有するポリオレフィンとしては、水素と炭素からだけからなるポリオレフィン系の樹脂で、なおかつ、主鎖骨格或いは側鎖に、結晶構造を阻害する環状構造、カサ高い構造等の因子が存在すれば良いが、主査骨格に環状ポリオレフィン成分を有するポリオレフィン系の樹脂「環状ポリオレフィン共重合体」が好ましく用いられる。

【０００７】環状オレフィン成分としては、例えばビシクロ（２．２．１）ヘプト－２－エンまたはその誘導体、テトラシクロ（４．４．０．$1^{2,5}$．$1^{7,10}$）－３－ドデセンまたはその誘導体、ヘキサシクロ（６．６．１．$1^{3,6}$．$1^{10,13}$．$0^{2,7}$．$0^{9,14}$）－４－ヘプタデセンまたはその誘導体、オクタシクロ（８．８．０．$1^{2,9}$．$1^{4,7}$．$1^{11,10}$．$1^{13,16}$．$0^{3,8}$．$0^{12,17}$）－５－ドコセンまたはその誘導体、ペンタシクロ（６．６．１．$1^{3,6}$．$0^{2,7}$．$0^{9,14}$）－４－ヘキサデセンまたはその誘導体、ペンタシクロ（６．５．１．$1^{3,6}$．$0^{2,7}$．$0^{9,13}$）－４－ペンタデセンまたはその誘導体、ヘプタシクロ（８．７．０．$1^{2,9}$．$1^{4,7}$．$1^{11,16}$．$0^{3,8}$．$0^{12,16}$）－５－ヘンエイコセンまたはその誘導体、トリシクロ（４．４．０．$1^{2,5}$）－３－ウンデセンまたはその誘導体、トリシクロ（４．３．０．$1^{2,5}$）－３－デセンまたはその誘導体、ペンタシクロ（６．５．１．$1^{3,6}$．$0^{2,7}$．$0^{9,13}$）－４，１０－ペンタデカジエンまたはその誘導体、ペンタシクロ（４．７．０．$1^{2,5}$．$0^{8,13}$．$1^{9,12}$）－３－ペンタデセンまたはその誘導体、ヘプタシクロ（７．８．０．$1^{3,6}$．$0^{2,7}$．$1^{10,17}$．$0^{11,16}$．$1^{12,15}$）－４－エイコセンまたはその誘導体、ノナシクロ（９．１０．１．$1^{4,7}$．$0^{3,8}$．$0^{2,10}$．$0^{12,21}$．$1^{13,20}$．$0^{14,19}$．$1^{15,19}$）－５－ペンタセコンまたはその誘導体をあげることができる。

【０００８】環状オレフィン成分を含有させるポリオレフィンの成分としては、例えば、エチレン、及びプロピレン、１－ブテン、１－ペンテン、４－メチル－ペンテン、３－メチル－ペンテン、１－ヘキセン、１－ヘプテン、１－オクテン、１－ノネン、１－デセン等をあげることができ、これら１成分からなるホモポリマーでも、２成分以上からなる共重合ポリマーでも良い。環状オレフィン成分を含有させた環状ポリオレフィン共重合体において、エチレン成分に由来する構造単位は４０～９５モル％、好ましくは５０～８０モル％の範囲、環状ポリオレフィン成分に由来する構造単位は１モル％添加から効果があるが、通常５～６０モル％、好ましくは２０～５０モル％の範囲が適当であり、エチレン成分等のオレフィン成分に由来する構造単位はランダムに配列し環状ポリオレフィン共重合体を形成している。

【０００９】また、前記環状ポリオレフィン共重合体を、ポリオレフィン系樹脂の間に介在させることにより、耐衝撃性に優れ、且つ成形性の良いポリオレフィン系樹脂を用いることにより、前記環状ポリオレフィン共重合体の持つ衝撃強度が小さく、また成形性が悪いという欠点を補うことができる。

【００１０】この前記環状ポリオレフィン共重合体を、中間層として介在させる、ポリオレフィン系樹脂としては、一般的なポリオレフィン樹脂、すなわちポリエチレン樹脂、ポリプロピレン樹脂、ポリメチルペンテン樹脂、ポリブテン樹脂、エチレン酢酸ビニル共重合体等にエチレン－αオレフィン共重合体または、プロピレン－αオレフィン共重合体を添加した樹脂、あるいはエチレン－αオレフィン共重合体または、プロピレン－αオレフィン共重合体の単体の樹脂等のポリオレフィン樹脂、

または、これらの２種類以上の混合物を用いることができる。

【００１１】本発明の多層構造物を利用する場合の具体的な構成はポリオレフィン系樹脂（Ａ）の間に環状オレフィンを有するポリオレフィン（Ｂ）が介在するようにする限り任意の配置をとることができ、例えば、下記（イ）の構成をとる。

（イ）Ａ／Ｂ／Ａの３層構成

【００１２】前記（イ）の層構成において、層間の接着性が乏しい場合には、樹脂層の間に接着性樹脂（Ｃ）を介在することもでき、この場合の接着性樹脂としては酸変性オレフィン樹脂、例えば無水マレイン酸、アクリル酸、メタクリル酸、無水イタコン酸等のエチレン系不飽和カルボン酸またはその無水物でグラフト変性されたポリエチレン、ポリプロピレン、エチレン－αオレフィン共重合体等の接着性樹脂、あるいはエチレン含有量９９～７０モル％のエチレンと、不飽和モノカルボン酸との共重合体、不飽和モノカルボン酸との共重合体の金属塩、不飽和モノカルボン酸エステルとの共重合体から選ばれる少なくとも１種の共重合体を介在させることができる。その場合環状オレフィンを有するポリオレフィン（Ｂ）に対して例えば、下記（ロ）の構成をとる。

（ロ）Ａ／Ｃ／Ｂ／Ｃ／Ａの５層構成

【００１３】耐衝撃性、耐熱性、及び水蒸気バリア性に加えて、酸素等のガスバリア性が要求される場合には、ガスバリア性樹脂（Ｄ）に対して例えば、下記（ハ）～（チ）の構成をとる。

（ハ）Ａ／Ｂ／Ｄ／Ａの４層構成

（ニ）Ａ／Ｂ／Ｄ／Ｂ／Ａの５層構成

（ホ）Ａ／Ｄ／Ｂ／Ａの４層構成

（ヘ）Ａ／Ｂ／Ａ／Ｄの４層構成

（ト）Ａ／Ｂ／Ｄ／Ａ／Ｄの５層構成

（チ）Ｄ／Ａ／Ｂ／Ａの４層構成

前記（ハ）～（チ）のガスバリア性樹脂（Ｄ）としては、多塩基酸と多価アルコールからなる共重合体または、それぞれ多塩基酸と多価アルコールに、コモノマー成分として他の多塩基酸および他の多価アルコール成分を含む共重合体や、エチレン含量が２５～６０モル％のエチレン－酢酸ビニル共重合体を、ケン化度が９６％以上にケン化して得られる共重合体や、炭素数１００個あたりのアミド基の数が３～３０個の範囲で含有されるホモポリアミド、コポリアミド、またはそのブレンド樹脂が好適に使用し得る。また前記した層構成において、層間の接着性が乏しい場合には、樹脂層の間に接着性樹脂を介在することもでき、この場合の接着性樹脂としては酸変性オレフィン樹脂、例えば無水マレイン酸、アクリル酸、メタクリル酸、無水イタコン酸等のエチレン系不飽和カルボン酸またはその無水物でグラフト変性されたポリエチレン、ポリプロピレン、エチレン－αオレフィン共重合体等の接着性樹脂を介在させることができる。

【００１４】本発明の防湿性多層構造物はスクラップ樹脂を介在することもでき、具体的には、スクラップ樹脂層（Ｅ）に対して下記（リ）、及び（ヌ）の層構成があげられる。

（リ）Ａ／Ｂ／Ｅ／Ａの４層構成

（ヌ）Ａ／Ｅ／Ｂ／Ｅ／Ａの５層構成

さらに、スクラップ樹脂層を含む構成において、前記したガスバリア性樹脂層を含む構成との組み合わせることもなんら差し支えはない。また層間の接着性が乏しい場合には、樹脂層の間に前記した接着性樹脂を介在することもできる。

【００１５】本発明の多層構造物をヒートシール等により製袋する場合の具体的な層構成として、基材層（Ｆ）としてシーラント層より熱変形温度の高い樹脂層、例えば、ポリエステル系樹脂、ポリアミド系樹脂、ポリカーボネート系樹脂、ポリアクリロニトリル系樹脂等が良好に使用できる。前記基材層は、一般的な押出ラミネート法（ドライラミネート、ウェットラミネート）による基材として、二軸延伸フィルムの構成であっても差し支えなく、例えばポリエステル系樹脂の場合、成形後縦方向に４～６倍、横方向に４～６倍二軸延伸して、二軸延伸後熱固定した二軸延伸ポリエステルフィルム等が好ましく用いられる。あるいは、基材層とも共押出であっても差し支えなく、更に、金属等で蒸着された基材層を用いてもなんら差し支えない。また、シーラント層構成中のポリオレフィン系樹脂は、一般的なポリオレフィン樹脂、すなわちポリエチレン樹脂、ポリプロピレン樹脂、ポリメチルペンテン樹脂、ポリブテン樹脂、エチレン酢酸ビニル共重合体等にエチレン－αオレフィン共重合体または、プロピレン－αオレフィン共重合体を添加した樹脂、あるいはエチレン－αオレフィン共重合体または、プロピレン－αオレフィン共重合体の単体の樹脂等のポリオレフィン樹脂あるいは、これらのブレンド樹脂等が使用でき、具体的には基材層（Ｆ）に対して下記（ル）の層構成があげられる。

（ル）Ｆ／Ａ／Ｂ／Ａ

前記（ル）の層構成において、層間の接着性が乏しい場合には、樹脂層の間に前記した接着性樹脂を介在することもでき、さらに前記したガスバリア性樹脂層を含む構成、加えて前記したスクラップ層を含む構成との組み合わせることもなんら差し支えはない。

【００１６】本発明における耐衝撃性に優れた防湿性多層押出構造物は、環状オレフィン成分５～６０モル％を有するポリオレフィンを、ポリオレフィン樹脂に介在させる３層構成を基本とし、前記したようなバリエーションを有し、層構成が対称であっても非対称であっても差し支えない。

【００１７】

【作用】本発明では、ポリオレフィン系樹脂層の間に、環状オレフィン成分５～６０モル％を有するポリオレフ

ィン樹脂層を介在させることにより、耐衝撃性に優れた防湿性多層押出構造物を提供可能とする。

【００１８】

【実施例】以下に本発明の実施例とその比較例を示す。

＜実施例１＞３本のスクリュー押出機を有する多層押出ブロー成形機を用いて、外層として、ポリエチレン樹脂、中間層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、内層としてポリエチレン樹脂の３層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００１９】＜実施例２＞３本のスクリュー押出機を有する多層押出ブロー成形機を用いて、外層として、ポリプロピレン樹脂、中間層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、内層としてポリプロピレン樹脂の３層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２０】＜実施例３＞３本のスクリュー押出機を有する多層押出ブロー成形機を用いて、外層として、ポリエチレン樹脂、中間層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；２０モル%，エチレン成分；８０モル%）樹脂、内層としてポリエチレン樹脂の３層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２１】＜実施例４＞３本のスクリュー押出機を有する多層押出成形機を用いて、外層として、ポリエチレン樹脂、中間層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、内層としてポリエチレン樹脂の３層構成、平均厚さ２ｍｍのシートを成形し、さらに真空成形により、胴部平均肉厚５００μｍ、内容積１００ｍｌのカップを成形した。

【００２２】＜実施例５＞３本のスクリュー押出機を有する多層延伸ブロー成形機を用いて、外層として、ポリプロピレン樹脂、中間層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、内層としてポリプロピレン樹脂の３層構成、胴部平均肉厚５５０μｍ、縦延伸倍率２．０倍、横延伸倍率２．３５倍、面倍率４．７０倍、表面積０．０５０m^2、内容積５００ｍｌのボトルを成形した。

【００２３】＜実施例６＞６本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第４層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第５層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第６層（最内層）としてポリエチレン樹脂の６層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２４】＜実施例７＞７本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第４層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第５層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第６層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第７層（最内層）としてポリエチレン樹脂の７層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２５】＜実施例８＞５本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層としてポリエチレン樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層（最内層）のガスバリア樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体の５層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２６】＜実施例９＞８本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第４層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第５層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第６層として、ポリエチレン樹脂、第７層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第８層（最内層）のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体の８層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２７】＜実施例１０＞５本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）のガスバリア樹脂として、エチレン含量が２５モル％のエチレン－酢酸ビニル共重合体を、ケン化度９６％にケン化して得られる共重合体、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層として、ポリエチレン樹脂、第４層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第５層（最内層）として、ポリエチレン樹脂の５層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２８】＜実施例１１＞５本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層の接着剤層としてエチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層としてエチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層（最内層）としてポリエチレン樹脂の５層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００２９】＜実施例１２＞４本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第４層（最内層）としてポリエチレン樹脂の４層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００３０】＜実施例１３＞７本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層の接着剤層としてエチレンとα－オレフィン共重合体の無水マレイン酸変性物、第４層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第５層の接着剤層としてエチレンとα－オレフィン共重合体の無水マレイン酸変性物、第６層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第７層（最内層）として、ポリエチレン樹脂の７層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００３１】＜実施例１４＞７本のスクリュー押出機を

有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第６層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第７層（最内層）としてポリエチレン樹脂の７層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００３２】＜実施例１５＞８本のスクリュー押出機を有する多層押出ブロー成形機を用いて、第１層（最外層）として、ポリエチレン樹脂、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第６層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第７層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第８層（最内層）としてポリエチレン樹脂の８層構成、胴部平均肉厚７５０μｍ、内容積８００ｍｌのボトルを成形した。

【００３３】＜実施例１６＞４本のスクリュー押出機を有する多層押出成形機を用いて、基材層（最外層）として、ポリエチレンテレフタレート樹脂、第２層樹脂としてポリエチレン樹脂、第３層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層（最内層）樹脂としてポリエチレン樹脂の４層構成、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００３４】＜実施例１７＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、３本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層樹脂として、ポリエチレン樹脂の３層構成のフィルムを、ドライラミネート法により張り合わせ、（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールによ

り、内容積２００ｍｌのパウチを製袋した。

【００３５】＜実施例１８＞あらかじめ、基材層にアルミ蒸着された、二軸延伸ポリエチレンテレフタレート樹脂構成フィルムと、３本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層樹脂として、ポリエチレン樹脂の３層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００３６】＜実施例１９＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、４本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第４層樹脂として、ポリエチレン樹脂の４層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００３７】＜実施例２０＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、５本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層樹脂として、ポリエチレン樹脂の５層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００３８】＜実施例２１＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、６本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第６層樹脂として、ポリエチレン樹脂の６層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００３９】＜実施例２２＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、６本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第４層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第５層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第６層樹脂として、ポリエチレン樹脂の６層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００４０】＜実施例２３＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、７本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第３層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第４層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第５層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第６層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第７層樹脂として、ポリエチレン樹脂の７層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μｍのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００４１】＜実施例２４＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、７本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層樹脂として、環状ポリ

オレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第６層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第７層樹脂として、ポリエチレン樹脂の７層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μmのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００４２】＜実施例２５＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、８本のスクリュー押出機を有する多層押出成形機を用いて成形された、第１層樹脂として、ポリエチレン樹脂、第２層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第３層樹脂として、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂、第４層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第５層のガスバリア性樹脂として、エチレン含量が２５モル%のエチレン－酢酸ビニル共重合体を、ケン化度９６%にケン化して得られる共重合体、第６層の接着剤層として、エチレンとα－オレフィン共重合体の無水マレイン酸変性物、第７層のスクラップ層として、ポリエチレン樹脂と、本実施例からなる多層構造物のスクラップ材を５０：５０重量比で混合した樹脂、第８層樹脂として、ポリエチレン樹脂の８層構成のフィルムを、ドライラミネート法により張り合わせ（ラミネート面は基材層と第１層の間）、平均厚さ２５０μmのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００４３】＜比較例１＞１本のスクリュー押出機を有するブロー成形機を用いて、ポリエチレン樹脂の単層構成、胴部平均肉厚７５０μm、内容積８００ｍｌのボトルを成形した。

【００４４】＜比較例２＞１本のスクリュー押出機を有するブロー成形機を用いて、ポリプロピレン樹脂の単層構成、胴部平均肉厚７５０μm、内容積８００ｍｌのボトルを成形した。

【００４５】＜比較例３＞１本のスクリュー押出機を有するブロー成形機を用いて、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂の単層構成、胴部平均肉厚７５０μm、内容積８００ｍｌのボトルを成形した。

【００４６】＜比較例４＞１本のスクリュー押出機を有する押出成形機を用いて、ポリプロピレン樹脂の単層構成、平均厚さ２mmのシートを成形し、さらに真空成形により、胴部平均肉厚５００μm、内容積１００ｍｌのカップを成形した。

【００４７】＜比較例５＞１本のスクリュー押出機を有する押出成形機を用いて、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂の単層構成、平均厚さ２mmのシートを成形し、さらに真空成形により、胴部平均肉厚５００μm、内容積１００ｍｌのカップを成形した。

【００４８】＜比較例６＞１本のスクリュー押出機を有する延伸ブロー成形機を用いて、ポリプロピレン樹脂の単層構成、胴部平均肉厚５５０μm、縦延伸倍率２．０倍、横延伸倍率２．３５倍、面倍率４．７０倍、表面積０．０５０m^2、内容積５００ｍｌのボトルを成形した。

【００４９】＜比較例７＞１本のスクリュー押出機を有する延伸ブロー成形機を用いて、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂の単層構成、胴部平均肉厚５５０μm、縦延伸倍率２．０倍、横延伸倍率２．３５倍、面倍率４．７０倍、表面積０．０５０m^2、内容積５００ｍｌのボトルを成形した。

【００５０】＜比較例８＞２本のスクリュー押出機を有する多層押出成形機を用いて、基材層（外層）として、ポリエチレンテレフタレート樹脂、内層としてポリプロピレン樹脂の２層構成、平均厚さ２５０μmのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００５１】＜比較例９＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、１本のスクリュー押出機を有する多層押出成形機を用いて成形された、環状ポリオレフィン共重合体（環状オレフィン成分；５０モル%，エチレン成分；５０モル%）樹脂の単層フィルムを、ドライラミネート法により張り合わせ、平均厚さ２５０μmのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００５２】＜比較例１０＞二軸延伸されたポリエチレンテレフタレート樹脂構成フィルムの基材層と、１本のスクリュー押出機を有する多層押出成形機を用いて成形された、ポリエチレン樹脂のフィルムを、ドライラミネート法により張り合わせ、平均厚さ２５０μmのフィルムを成形し、さらにヒートシールにより、内容積２００ｍｌのパウチを製袋した。

【００５３】以上の結果を（表１）、（表２）に示す。（評価方法）　落下衝撃強度については、容器１０個に水を満水まで充填し、５℃に１２時間保存後、正立状態でコンクリート上に１mの高さより、１０回自由落下させた場合の割れ本数を測定した。透湿度については、ＪＩＳ　Ｚ０２２２に準拠した透湿度測定を行った。

【００５４】

【表１】

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	落下衝撃強度（破損個数）	透湿度（mg／pkg－30days）
実施例1	0	205
実施例2	0	198
実施例3	0	201
実施例4	0	146
実施例5	0	87
実施例6	0	195
実施例7	0	176
実施例8	0	202
実施例9	0	199
実施例10	0	203
実施例11	0	209
実施例12	0	214
実施例13	0	197
実施例14	0	205
実施例15	0	192
実施例16	0	479
実施例17	0	499
実施例18	0	101
実施例19	0	498
実施例20	0	571
実施例21	0	582
実施例22	0	573
実施例23	0	475
実施例24	0	596
実施例25	0	587

【００５５】（表１）は、各実施例で得られた容器の物性を示す。

＊【００５６】
＊　【表２】

	落下衝撃強度（破損個数）	透湿度（mg／pkg－30days）
比較例1	0	610
比較例2	0	650
比較例3	10	200
比較例4	0	470
比較例5	10	151
比較例6	0	385
比較例7	10	179
比較例8	0	1910
比較例9		410
比較例10		1830

【００５７】（表２）は、各比較例で得られた容器の物性を示す。

【００５８】

【発明の効果】本発明の方法によると、ポリオレフィン系樹脂層の間に、環状オレフィン成分５～６０モル％を※有するポリオレフィン樹脂層を介在させることにより、物性及び、成形性等の点において良好で、耐衝撃性に優れ、更に従来のポリオレフィン系樹脂よりも、防湿性に優れた多層押出構造物およびそれを用いた防湿性に優れた多層容器を得ることが可能となる。

フロントページの続き

(72)発明者　加藤　俊一
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